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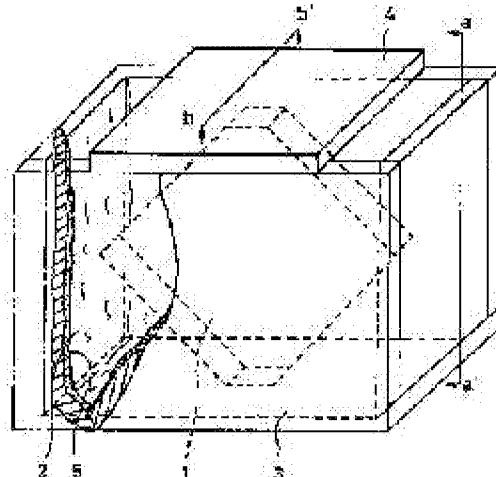
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(54) PRODUCTION OF REACTION INJECTION MOLDED PRODUCT

(57)Abstract:

PURPOSE: To enhance the molding efficiency of a molded product having a hollow part by arranging a foamed object molded from a solvent-soluble or hot-melt polymer in a mold as a core and supplying a reactive liquid raw material into the mold to mold a reaction injection molded product and taking out the molded product from the mold before removing the core by solvent treatment or heat treatment.

CONSTITUTION: A foam core 1 molded from a solvent-soluble or hot-melt polymer is arranged in a mold wherein an aluminum foil 5 is bonded to the inner surface of a wood mold formed from a wood retaining mold 3. A reactive solution 2 prepared by mixing a plurality of reactive raw materials is introduced into the mold and cured to obtain a molded product having a hollow part. The core of the molded product taken out of the mold is dissolved by a solvent or melted by a heating means 1 to be removed. Therefore, the molding efficiency of the molded product is improved.



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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Industrial Application]This invention relates to the manufacturing method of mold goods with undercut shape or a centrum. It is related with the manufacturing method of the mold goods by reaction shaping which manufactures mold goods with undercut shape or a centrum efficiently by removing in more detail the core of the foam fabricated to resin (following matrix) and one at the time of shaping from mold goods with heating or a solvent after shaping.

[0002]

[Description of the Prior Art]Generally the method of supplying a reactant liquid raw material in the mold which has arranged the core, polymerizing within a mold, and manufacturing mold goods with reaction shaping, is the well-known method. after [for example,] installing the core made of silicone rubber in a mold and carrying out reaction injection molding (henceforth, RIM) to JP,1-247123,A -- this -- a core is drawn out and the method of manufacturing hollow products is indicated.

[0003]It became possible to manufacture mold goods with a complicated centrum with sufficient productivity by one by this invention. However, this manufacturing method has the problem that it cannot be used in the product of the shape which cannot draw out a core.

[0004]In the mold which made JP,3-266743,A support the core which consists of thermofusion nature or a water-soluble material, heating after introducing and fabricating melting nature material, or water -- a core -- it introduces inside and melting or the method of making it dissolve, beginning to pass from mold goods, and fabricating the bumper beam made of resin is indicated in the core.

[0005]Restrictions become there are not in the shape of a core less, and this invention enabled it to also manufacture mold goods with a complicated-shaped centrum. For this reason, the manufacturing process became it is also possible to take undercut shape freely and simple,

and the rate of productivity increased. However, at the time shown in this gazette example, since the core of low melting point metallicity is heavy, operativity has difficulty, and. Melting of the low melting point metal is carried out, and when manufacture a core, or keeping it until it uses the core for shaping, or taking out from mold goods, there is a problem that the treatment of metal after carrying out melting becomes serious. When it becomes large-sized also by the core made from a plastic, the weight of itself becomes quite heavy, operativity has difficulty, and also by a core small [even if], when making it dissolve with water or carrying out melting with heating, there is a problem of taking time dramatically.

[0006]

[Problem(s) to be Solved by the Invention]The purpose of this invention supplies a reactant liquid raw material in the mold which has arranged the core, and there is in providing the method for fabricating mold goods with undercut shape or a centrum efficiently in the manufacturing method of the reaction-injection-molding article polymerized within a mold.

[0007]

[The means for solving an invention] In the manufacturing method of the reaction-injection-molding article which the purpose of this invention supplies a reactant liquid raw material in the mold which has arranged the core, and is polymerized within a mold, After using as a core the foam fabricated by polymer of soluble or thermofusion nature by the solvent, mold goods are picked out from a mold and it is attained by removing a core by solvent treatment or heat-treatment.

[0008]Hereafter, this invention is explained in detail.

(Reaction shaping) Reaction shaping is the method of using as a reaction stock solution the liquid raw material which consists of a monomer, a catalyst system, a hardening agent, etc. with a stable gestalt, if independent, and mixing the flow of two or more reaction stock solutions using a mixer or the mixed power by collision, making produce a chemical reaction, and fabricating mold goods.

[0009]In reaction shaping of reaction injection molding (RIM), RTM, casting, etc., etc., the reaction stock solution of hypoviscosity is made to react within a metallic mold, and various plastic molding is manufactured. According to the technical progress of this field, the range of applicable resin, such as norbornene system polymer, an epoxy resin, polyurethane resin, Nylon, unsaturated polyester resin, polyurea resin, and phenol resin, is also expanded.

[0010](Reaction molding raw material) The molding raw material concerning this invention should just be a raw material currently used for reaction shaping, and limitation in particular is not carried out.

[0011]Specifically A norbornene system, an epoxy system, a urethane system, a nylon system, A monomer or prepolymers, such as an unsaturation polyester system, a urea system, and a phenol system, are mentioned, To these, carry out initial-complement addition of a catalyst,

cocatalyst, a hardening agent, a reaction accelerator, a vulcanizing agent, the reaction modifier, etc., and also. According to the purpose, titanium oxide, calcium carbonate, aluminium hydroxide, talc, Refining material, such as colorant, such as bulking agents, such as carbon black, various paints, and a color, an antioxidant, an ultraviolet ray absorbent, an antifogger, a spray for preventing static electricity, fire retardant, dicyclopentadiene system petroleum resin, an adhesive improver like the hydrogenation thing, is added and used.

[0012]For example, if the reaction stock solution containing a norbornene system monomer and a metathesis catalyst system is supplied in a metallic mold and massive ring opening polymerization is carried out, a norbornene system polymer molded article will be obtained. If the reaction stock solution containing an isocyanate is made to react to polyol within a metallic mold, polyurethane resin mold goods will be obtained. The nylon RIM which similarly uses a polyester amide prepolymer and caprolactam as a reaction stock solution, The polyester RIM etc. which use as a reaction stock solution the epoxy RIM and unsaturated polyester which use an epoxy compound and hardening agents, such as polyamine and polyamide, as a reaction stock solution, a vinyl monomer, and a catalyst are mentioned.

[0013]Also in these shaping of norbornene system polymer by the RIM method, Since injection pressure is remarkable and low compared with injection molding of usual thermoplastics, it is desirable although the mold goods of an insert molded part, large-sized mold goods, and complicated shape are manufactured, since a cheap and lightweight metallic mold can be used, and the mobility of the raw material within a metallic mold is good. Then, the norbornene system RIM is explained further in full detail.

[0014]The norbornene system monomer used in norbornene system monomer this invention, As long as it has a norbornene ring, any may be sufficient, but if the polycyclic norbornene system monomer of three or more ring formations is used, the heat resistance which a polymer with high heat deflection temperature is obtained, and is demanded as a composite molding body can be filled. moreover -- the ring-opening-polymerization object to generate can be used as a heat-hardened type in this invention -- for that purpose -- the inside of total monomers -- 30% of the weight or more of a cross-linking monomer may be used preferably at least 10% of the weight.

[0015]As an example of a norbornene system monomer, two ring formations, such as norbornene and norbornadiene, Three ring formations, such as a dicyclopentadiene and a dihydrodicyclopentadiene, Five ring formations, such as four ring formations, such as tetracyclo dodecen, and tricyclo pentadiene, Seven ring formations, such as tetracyclo pentadiene, these alkylation objects. (For example, methyl, ethyl, propyl, a butyl substitution product, etc.), and alkenyl substitution products. The substitution product etc. which have polar groups, such as (for example, a vinyl substitution product), etc. alkylidene substitution products (for example, ethylidene substitution product etc.), aryl substitution products (for example,

phenyl, toyl, a naphthyl substitution product, etc.), an ester group, an ether group, a cyano group, and a halogen atom, are illustrated. These monomers may be used combining one or more sorts. Especially, the object for prizes of three ring formations thru/or the five ring formations is carried out from standpoints, such as an ease of acquisition, reactivity, and heat resistance.

[0016]A cross-linking monomer is a polycyclic norbornene system monomer which has two or more reactant double bonds, and a dicyclopentadiene, tricyclo pentadiene, tetracyclo pentadiene, etc. are illustrated as the example. Therefore, when a norbornene system monomer and a cross-linking monomer are the same things, it is not necessary to use the cross-linking monomer of exceptionally others.

[0017]Monocycle cycloolefins etc. which can carry out ring opening polymerization with one or more sorts of the above-mentioned norbornene system monomer, such as cyclobutene, cyclopentene, a cyclopentadiene, cyclooctane, and cyclo dodecen, can be used together in the range which does not spoil the purpose of this invention.

[0018]Any may be sufficient as long as the catalyst of a metathesis catalyst system to be used is a metathesis catalyst system which consists of a metathesis catalyst and an active agent publicly known as a catalyst for ring opening polymerization of a norbornene system monomer, As an example, halogenides, such as tungsten, molybdenum, and tantalum, The metathesis catalyst of a oxy halogenide, an oxide, organic ammonium salt, etc. is mentioned, and as an example of an active agent (cocatalyst), Alkylaluminum halide, alkoxy alkylaluminum halide, aryloxy alkylaluminum halide, an organotin compound, etc. are mentioned.

[0019]A metathesis catalyst is usually preferably used in the range of 0.1 to 20 millimol about 0.01 to 50 millimol to 1 mol of a norbornene system monomer. An active agent is preferably used in 1-10 (mole ratio) to a catalyst component. Although it is more desirable to dissolve and use for a monomer, as long as each of metathesis catalysts and active agents is ranges which do not spoil the character of output in essence, it may be made to suspend or dissolve in a little solvents, and they may be used for them.

[0020]In the desirable manufacturing method of norbornene system polymer, generally, a norbornene system monomer is divided into 2 liquid, and it puts into another container, and a metathesis catalyst is added to one side, an active agent is added in another side, and two kinds of stable reaction mixture is prepared. Two kinds of this reaction mixture is mixed, subsequently to the inside of the metallic mold of specified shape, or a mold (both are doubled and it is called a metallic mold) it pours in, and ring opening polymerization by massive is performed there.

[0021](Core) A core is formed by the foam fabricated by polymer of soluble or thermofusion nature by the solvent. As for a core, 1.5 to 30 times as much foam is preferably used for expansion ratio still more preferably 1.2 to 60 times 1.1 to 100 times. When expansion ratio is

low, the dissolving operation by a solvent takes time and the solvent to be used is also needed for a large quantity. If expansion ratio is high, will change, without the ability of a core to bear the resin pressure at the time of shaping, or it will destroy, or will float at the time of reaction mixture pouring.

[0022]As construction material, although thermoplastic polymer is used, the polymer which polymerization inhibition nature does not have at the time of the polymerization of a matrix raw material does not make mold goods generate smeariness, but since there are few unreacted monomer smells, it is usually more desirable. It is not preferred to use soluble foam for reaction mixture as a core. In order to prevent a core from preventing polymerization inhibition of reaction mixture or dissolving by reaction mixture, If required, the polymer which does not have polymerization inhibition nature in the portion which hits the interface of a matrix raw material and a core, and polymer which is hard to dissolve in reaction mixture can be applied by the spray or a brush, or a film can be twisted around a core, polymerization inhibition of an interface can be lessened, and it can also fabricate. As a finishing agent of this core, adhesives, such as a vinyl acetate system, a rubber system, a hydrocarbon system, a urethane system, an epoxy system, and a phenol system, a paint, a coating agent, a film, etc. are mentioned.

[0023]Polymer with the structure of cross linkage can also be used as a core, if promptly decomposed by the solvent. To a core, a bulking agent may be added and fabricated so that it may be easy to dissolve in a solvent. As a bulking agent used, although powder, such as carbon black, calcium carbonate, alumina, and kaolin, is mentioned, it is not limited to this. As long as the thickness of a core is thick and work is possible, after removing a core as much as possible using a knife or a hand, a solvent and heat treatment may be performed.

[0024]the core dissolved and removed with a solvent -- the core dissolved and removed with a solvent -- the heat deflection temperature -- usually -- not less than 50 ** not less than 30 ** is a not less than 80 ** thing still more preferably more preferably. If heat deflection temperature is low, by neither a mold temperature nor the reaction fever at the time of shaping, a core will change and the mold goods of desired shape will be obtained. If easily dissolvable to a solvent, heat deflection temperature is so preferred that it is high.

[0025]As an example of the raw material for forming a solvent solubility core, Polyethylene, polypropylene, polyvinyl acetate, an ethylene-vinylacetate copolymer, The copolymer of polystyrene, and a maleic anhydride and styrene, ABS plastics, Polyvinyl chloride, poly norbornene system resin, a polyvinyl pyrrolidone, A polyvinyl formal, a polyvinyl butyral, polyvinyl ether, Polycellulose acetate, polyacrylic acid, polyacrylic ester, polyethylene terephthalate, Polybutylene terephthalate, polymethacrylic acid, polymethacrylic acid ester, Resin, such as polyurethane, polybutadiene, polyisoprene, polychloroprene, A styrene butadiene copolymer, styrene Butadiene Styrene, a styrene isoprene styrene copolymer, a

poly norbornene system elastomer, and polyurethane system elastomers are mentioned -- water solubility, although polyvinyl alcohol, a polyvinyl pyrrolidone, gelatin, etc. are mentioned as an example for forming a core, It is not necessarily limited to these.

[0026]From points, such as polymerization inhibition nature, moderate heat resistance, the ease of carrying out of the dissolution to a solvent, and an ease of acquisition. The core of polyethylene, polypropylene, polyvinyl acetate, an ethylene-vinylacetate copolymer, polystyrene, ABS plastics, and polyvinyl chloride is preferred, and the core of polyethylene, an ethylene-vinylacetate copolymer, polystyrene, and ABS plastics is still more preferred. .the core from the field of safety -- since there are little ease of processing after the dissolution, and inflammability and toxic danger, it is preferred to use the core of construction material which dissolves with water.

[0027]the core removed with heating -- the core removed with heating -- the heat deflection temperature -- usually -- 30 ** - 150 ** (40 ** - 130 **) are 50 ** - 110 ** still more preferably more preferably. If heat deflection temperature is too low, a core will change with a mold temperature or the reaction fever at the time of shaping, if heat deflection temperature is too high, cooking temperature must be raised to near the glass transition temperature of a matrix, and it comes to take time the operation which modification of mold goods' own contraction, curvature, etc. arises, or fuses and removes a core.

[0028]As an example of the core taken out with heating, polyethylene, polypropylene, The copolymer of polyvinyl acetate, an ethylene-vinylacetate copolymer, polystyrene, and a maleic anhydride and styrene, ABS plastics, polyvinyl chloride, poly norbornene system resin, a polyvinyl pyrrolidone, Polyvinyl ether, polycellulose acetate, polyacrylic ester, Polymethacrylic acid ester, polyethylene terephthalate, polybutylene terephthalate, Resin, such as polyurethane, polybutadiene, polyisoprene, polychloroprene, Although a styrene butadiene copolymer, styrene Butadiene Styrene, a styrene isoprene styrene copolymer, a poly norbornene system elastomer, and polyurethane system elastomers are mentioned, it is not necessarily limited to this.

[0029]How to remove the core which dissolving and removing with a solvent can also remove with heating is suitably determined by the shape of equipment or a core, and the size. Although operation until the method which uses a solvent generally takes out a core can be taken out finely early, To disposal of the treating solution after taking out being needed, the method by heating will need time, by the time a core is heated, and while it must remove while the core is fusing, and it must be operated, there is an advantage that the removed core can be disposed of as it is.

[0030]The core of polyethylene from the ease of polymerization inhibition nature, moderate heat resistance, and acquisition, polypropylene, polystyrene, ABS plastics, and polyvinyl chloride is preferred.

[0031]When removing the core which dissolving and removing with a solvent can also remove with heating, said two sorts of methods can also be used together. As this mode, most cores are fused with heating, the method of probing a retained material with a solvent and the heated core are probed with a solvent (non-molten state), for example, and how to shorten processing time can be considered.

[0032](Manufacturing method of a core) What was fabricated separately is used for a core by foaming. In the foam means of foam, ** volatile fluid and the fluid of resolvability are added in a raw material. ** Blow gases, such as air and nitrogen, into a raw material. ** Make a raw material foam with a spray. ** Make a raw material foam using reactant gas. ** After dissolving in soluble matter, there is the method of removing this soluble matter. Foam is fabricated combining art, such as injection molding and extrusion molding, to these foam means.

[0033]For example, after being quickly filled up with a small amount of resin, and making it foam from the capacity of a cavity or carrying out injection fill of the high-pressure resin, a movable side metallic mold is retreated and there are a method etc. to which expand cavity capacity and it is made to foam. The foam in which the foam fabricated by the latter method has what is called a skin as which foaming is hardly regarded on the surface is obtained.

[0034]If foam with such a skin is used as a core, matrix resin will not sink into foam, Even when there is matrix polymerization inhibition, while an interface with a matrix can fabricate smoothly and being able to lessen [smell / unreacted / residual monomer], The air bubbles inside foam expand with the reaction fever at the time of a polymerization, and in order to push a matrix for a mold face, mold goods have an advantage of not producing HIKE.

[0035]Although the method of carrying out foaming using the bead made from foaming of polystyrene and the method of carrying out foaming with the paste of vinyl chloride are mentioned in addition to this, it is not necessarily limited to these methods.

[0036](Base material of a core) The synthetic resin dissolved and fused by neither a solvent nor heat-treatment at a core if required, The base material formed in metal, wood, etc. can be formed in the desired part of a core, and a core can be prevented from floating by reaction mixture within a metallic mold, and a gap can be provided between a core and a metallic mold inner surface, and a uniform resin layer can be made to form as an outer peripheral layer. As shape of a base material, various forms, such as a cylindrical shape, plate-like, a cone form, and a conical trapezoid, can be taken. In order to form a base material, there are proper methods, such as pasting up a base material on the surface of a core, fixing, or using the shape of a rubber band and twisting.

[0037](Metallic mold) What was created with various materials, such as various synthetic resins, aluminum, low melting alloys, a tree, and iron, can be used for a metallic mold, and it may be a mere mold.

[0038](Process condition) It is a molding method which reaction shaping transports two or

more reaction raw materials to a mixer independently, it mixes each raw material by mixing through mixed devices, such as a power mixer and a static mixer, and collision mixing, and makes it reaction mixture, draws this reaction mixture into a metallic mold, stiffens it, and obtains mold goods.

[0039]although a general forming process changes with forming processes -- casting -- in 1 - 5 kg/cm² and RTM, as for a mixed pressure, injection pressure carries out collision mixing of the mixed pressure by 50 - 150 kg/cm² at 5 - 50 kg/cm² and reaction injection molding. A suitable forming process and a process condition are chosen according to descriptions, such as a kind of material, and viscosity.

[0040]The activity of reaction mixture also uses it according to the size of mold goods, or the filling speed of a raw material, changing the quantity of a catalyst system or a hardening agent suitably. Although the time of one cycle is adjusted in 5 or less minutes in many cases, 1 hour may be surpassed and limitation in particular is not carried out.

[0041]A collision mixing device publicly known as a RIM molding device from the former in this invention can be used in order to mix two kinds of reaction stock solutions. In this case, the container which stored two kinds of reaction stock solutions serves as a supply source of a separate flow. Two kinds of flows are momentarily mixed by the mixing head of a RIM opportunity, and it ranks second, and pours in into a metallic mold, mass polymerization is carried out immediately there, and mold goods are obtained.

[0042]Besides a collision mixing device, low-pressure potting machines, such as a dynamic mixer and a SUTACHIKKU mixer, can also be used. When there is pot life in a room temperature for as long as 1 hour, after mixing of two kinds of reaction solutions is completed in a mixer, it may eject or pour in several times into the metallic mold which carried out preheating, and may pour in continuously. When in the case of this method can miniaturize a device as compared with a collision mixing device, it has the advantage of being operational, with low pressure and also there are many fill ratios of bulking agents, such as glass fiber, it becomes possible by carrying out transfer speed slowly to impregnate with reaction mixture uniformly in a system.

[0043]In this invention, it is not limited to the method of using two kinds of reaction stock solutions. If it is a person skilled in the art, various kinds of modification, such as putting the additive agent of a monomer and a request into the third container, and using it as the third flow, is possible so that he can understand easily.

[0044]Although reaction mixture is usually stored and operated under inert gas atmospheres, such as nitrogen gas, it is not necessary to necessarily carry out the seal of the forming mold with inactive gas. A die temperature is set up between 30 ** (room temperature) - 200 ** in many cases. the effect of promoting a polymerization reaction, and the capability to absorb generation of heat at the time of hardening serve as a die temperature, and it suits, and is

come out of and determined.

[0045]Below, the case of the massive ring opening polymerization of a norbornene system monomer is explained in full detail.

40-200 ** of massive ring-opening-polymerization die temperatures of a norbornene system monomer of usual and beyond a room temperature are 50-130 ** especially preferably preferably. As for the ingredients used for a polymerization reaction, it is preferred to store and operate it under inert gas atmospheres, such as nitrogen gas. The pressure in a metallic mold is a 0.1 - 10 kg/cm² grade, and polymerization time is shorter than 20 minutes, and is usually less than 5 minutes preferably.

[0046]Additive agents, such as an antioxidant, a filler, a reinforcing member, a foaming agent, paints, colorant, and an elastomer, can be blended with norbornene system polymer. Although reaction mixture is dissolved or distributed and these additive agents are usually blended with it, they may be allocated in the metallic mold.

[0047]As an elastomer added to reaction mixture, for example Crude rubber, polybutadiene, Polyisoprene, a styrene butadiene copolymer (SBR), styrene butadiene styrene block copolymer (SBS), A styrene isoprene styrene copolymer (SIS), an ethylene-propylene-diene terpolymer (EPDM), ethylene-vinylacetate copolymers (EVA), these hydrides, etc. are mentioned. If these elastomers are added to reaction mixture, shock resistance can not only be given to the polymer obtained, but it can adjust the viscosity of reaction mixture.

[0048](How to remove a core) The mold goods picked out from the mold remain into mold goods with the gestalt as it is at the time of a metallic mold set, when the heat deflection temperature of a core is higher than the reaction fever at the time of the polymerization of a matrix enough. When the heat deflection temperature of a core is low, selectively or on the whole, it fuses with the reaction fever at the time of the polymerization of a matrix. Also by such a core, it is removed from mold goods by a solvent or heating.

[0049]When using a solvent, according to the used core, a core is dissolved with the solvent which carries out easily dissolvable [of the core]. It is not preferred to use the solvent which invades a matrix. Since the core has exposed outside the portion fixed to the metallic mold, it pours in a solvent from this portion and dissolves the core. Since a core will be outside exposed if a base material is removed when it equips with a base material, a solvent is poured in from this portion and a core is dissolved. The liquid which dissolved polymer can be taken out from the portion which poured in the solvent.

[0050]Because a core fabricates with reaction fever when fabricating in the shape which has appeared from the mold-goods surface in convex when the existing foam of the heat resistance of the grade which is not fused is used and it is made mold goods. Even if it accumulates mold goods, between mold goods, a crevice is made, and mold goods do not contact and rub, but they can be accumulated so that conveyance and storage can be

performed without giving a crack to the surface, or it can insert in and put upon the portion fabricated to the concave. In this case, what is necessary is just to work by a core removing on the spot just before use. This method is the very efficient method of preventing generating of inferior goods while saving the time and effort of the package at the time of conveyance.

[0051]a solvent -- the operation of soluble which melts a core with a solvent and is removed is so easy to a solvent in a core that it means that a core dissolves for a short time at a room temperature at a solvent and is soluble.

[0052]As an example of a solvent, water, formic acid, acetic acid, an acetic anhydride, alkali, pentane, Hexane, heptane, isoheptane, isooctane, industrial gasoline, Petroleum ether, petroleum benzine Cyclohexane, a methylcyclohexane, Benzene, xylene, solvent naphtha, a decalin, creosote oil, Hydrocarbon system solvents, such as turpentine, a methylene chloride, chloroform, a carbon tetrachloride, Dichlorofluoromethane, an ethyl chloride, 1,2-dichloroethane, 1,2-dibromoethane, Tetrachloroethane, a dichloroethylene, trichloroethylene, perchloroethylene, Halogenated hydrocarbon systems, such as dichloropropane, amyl chloride, and monochlorobenzene, Methanol, ethanol, isopropyl alcohol, n-butyl alcohol, T-butyl alcohol, fusel oil, benzyl alcohol, ethylene glycol, Alcohols solvents, such as ethylene glycol monomethyl ether and ethyleneglycol dimethyl ether, Ethers solvents, such as ethyl ether, isopropyl ether, n-butyl ether, an anisole, dioxane, and a tetrahydrofuran, methyl formate, ethyl formate, butyl formate, methyl acetate, ethyl acetate, Ester solvents, such as isopropyl acetate, amyl acetate, and ethyl propionate, Methylal, an acetal, acetone, methyl ethyl ketone, methyl isobutyl ketone, An aldehyde system solvent and ketones, such as an acetylacetone and cyclohexanone, Nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, Nitrobenzene, acetonitrile, diethylamine, triethylamine, Nitrogen-containing compounds, such as ethylenediamine, pyridine, monoethanolamine, and dimethylformamide, Alkali, such as inorganic acid, such as chloride, sulfuric acid, etc. besides various organic solvents, such as sulphur-containing compounds, such as carbon bisulfide, a thiophene, and dimethyl sulfoxide, and these mixtures, sodium hydroxide, and a potassium hydrate, and these mixtures are mentioned.

[0053]Although it can be used according to the construction material of a core, and the workability and work environment to be used, choosing from these solvents suitably, what is easy to dissolve resin used as a matrix is not preferred. If resin used as a matrix is polymer of cross-linking, unless very severe swelling is carried out, consideration at this point is unnecessary, but in thermoplastic polymer, resin used as a matrix needs to be cautious of this point, and needs to choose a solvent.

[0054]When an organic solvent is used, after removing the polymer which dissolved in the solvent with the precipitation reagent or the flocculating agent, the reuse of the solvent can also be collected and carried out by distillation etc.

[0055]If it is polymer, such as polyvinyl alcohol, a polyvinyl pyrrolidone, and gelatin, specifically Water, Warm water; Again The copolymer of polyethylene, polypropylene, polystyrene, and a maleic anhydride and styrene, If ABS plastics etc. become, and it is solvent; polyvinyl ether of hydrocarbon systems, such as toluene, xylene, and a decalin, methanol, Acetone; If it is polyvinyl chloride, cyclohexanone, nitrobenzene, A tetrahydrofuran, pyridine, butyl acetate, a dichloroethane, methyl isobutyl ketone, etc.; If it is cellulose acetate and is an acetone; polyacrylic ester system and a polymethacrylic acid ester system, acetone, Ethyl acetate, dichloroethane, benzene; If it is polyurethane, sulfuric acid, Formic acid etc.; toluene will be mentioned if it is elastomers, such as polybutadiene, polyisoprene, polychloroprene, a styrene butadiene copolymer, styrene Butadiene Styrene, a styrene isoprene styrene copolymer, and polyurethane.

[0056]These solvents should just use suitably the core to be used and the solvent which is easy to treat according to the kind of matrix resin. Working hours can be shortened by heating and using a solvent at the time of use.

[0057]As a method of fusing a core with heating method heating and removing, After it settles the whole mold goods on the oven and thermostatic chamber of specified temperature and a core fuses on the whole, this -- a core -- although the method of pressing against a core directly the metal stick etc. which were heated beyond the heat-resistant temperature of resin of the method of removing an ingredient or a core, and fusing a core, or the method of fusing only resin of a core by high frequency or electromagnetic waves is raised, it is not limited to this. Since the core is fusing at the time of mold-goods unmolding when the heat deflection temperature of a core is lower than the polymerization reaction heat of a matrix enough, the core fused as it was can be removed.

[0058]

[Effect]According to this invention, a reactant liquid raw material is supplied in the mold which has arranged the core, and the method for fabricating mold goods with undercut shape or a centrum efficiently is provided in the manufacturing method of the reaction-injection-molding article polymerized within a mold.

[0059]

[Example]An example is given to below and this invention is explained to it still more concretely. The part in an example is a weight reference as long as there is no notice especially.

[0060][Example 1] The board of with a twice as many expansion ratio [as this] polystyrene foam was started with the knife on a 10-cm square at 2 cm in thickness, 2 cm was further cut off from the two angles which counter, and the core of shape as shown in drawing 1 was created. this -- a core is set in the center of a mold, main ** of a metal plate is put on the upper part, and the core was kept from floating A mold is inside dimension, and stuck and created

aluminum foil to the inner surface with the width 20 cm in width, 14 cm in height, and a depth of 6 cm wooden form.

[0061]Said mold 3 which set the core was heated at 60 ** in oven.

[0062]On the other hand, a dicyclopentadiene (DCP) and methyltetracyclo dodecen (MTD) to 100 copies of mixed monomers mixed by the weight ratio of 9:1. 6.5 copies of styrene isoprene styrene block copolymers (SIS) (the Queen tuck 3421, the Nippon Zeon Co., Ltd. trade name) were added, and it mixed. This liquid was put into two containers, and to one side, to the mixed monomer, the diethylaluminium chloride (DEAC) was added, respectively so that it might become 41 millimol concentration about 41 millimol concentration and n-propyl alcohol and might become 21 millimol concentration about tetrachlorosilane (A liquid).

[0063]In another side, to the mixed monomer, the Tori (tridecyl) AMMONIMU molybdate was added so that it might become 10 millimol concentration, and on it, four copies of phenolic antioxidants per 100 copies of mixed monomers (made in [ethyl corporation company] Etah Knox 702) were added further (B liquid).

[0064]Both reaction mixture (mixture ratio 1/1 of A liquid / B liquid) was mostly poured in promptly to the undersurface of main ** by ordinary pressure using the gear pump and the power mixer into the aforementioned mold. The polymerization reaction was performed for about 3 minutes after pouring, and mold goods were obtained. Fusing the core with the heat of polymerization, foam remained only the part. Shortly after filling polystyrene of the core with toluene, it dissolves immediately and it was able to be begun to pass polystyrene from mold goods. The integrally molded product in the air was obtained.

[0065][Comparative example 1] Mold goods were fabricated like Example 1 except using for a core the sheet which is not foamed [of polystyrene]. The unfoamed sheet pasted together and created two 1-mm-thick things with commercial adhesive for plastic.

[0066]Although a part of interface with a matrix was fusing the core with the heat of polymerization, it remained mostly with the original form. toluene -- a core -- flowing into a portion -- a core -- the portion was dissolved. Although the core dissolved in toluene, 30 minutes or more were taken to dissolve all cores.

[0067][Example 2] It experimented like Example 1 except having changed to with a twice as many expansion ratio [as this] polystyrene foam, and having used the polyvinyl chloride 1.5 times the expansion ratio of this. The core was not fused with reaction fever.

[0068]The metal stick heated at 120 ** was pushed against the core, and the core was fused and removed. The time for about 5 minutes was taken to take out a core.

[Translation done.]